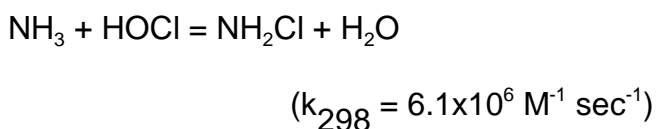


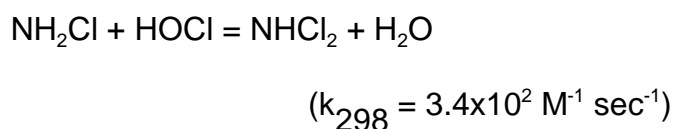
II. PHYSICAL AND CHEMICAL PROPERTIES

Introduction

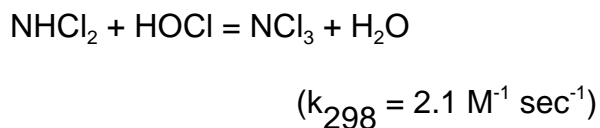
Inorganic chloramines are alternate disinfectants that are rapidly formed when free chlorine is added to water containing ammonia. This reaction is represented by the following equation with its respective reaction rate constant (at 25°C = 298°K) (Morris, 1967):



Since ammonia has more than one hydrogen that can be replaced by a chlorine atom, it reacts with an excess of hypochlorous acid to form dichloramine (Morris, 1967; Gray et al., 1979):



or trichloramine (Morris and Isaac, 1983):

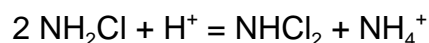


The distribution of mono-, di- and trichloramine is dependent on pH, temperature and relative concentrations of ammonia and hypochlorite as described in the following section on physical and chemical properties.

Physical and Chemical Properties of Chloramines

Under the usual conditions of water and wastewater chlorination, monochloramine is the principal chloramine encountered. Anhydrous monochloramine is a colorless, water-soluble liquid (Kirk-Othmer, 1979) that freezes at -66°C . The pure liquid decomposes above -50°C with formation of nitrogen, chlorine and nitrogen trichloride (Colton and Jones, 1955; Kovacic et al., 1970). The known chemical and physical properties of pure monochloramine are summarized in Table II-1. The environmental significance of monochloramine, however, is generally restricted to its aqueous solutions, where it is useful in water treatment for destruction of pathogenic bacteria (Butterfield, 1948; Wolfe et al., 1984). The rate of its formation is so rapid that determination of rates between pH 6.5 and 10 were impossible because of the rapidity of the reaction in this range (Weil and Morris, 1949). At pH 8.5 the rate of its formation reaction reaches a maximum (Weil and Morris, 1949). Monochloramine is the only chloramine formed when the pH of ammonia containing water is >8 and the molar ratio of hypochlorite to ammonia is <1 (Gray et al., 1979).

At hypochlorite to ammonia ratios >1 or at lower pH values, dichloramine and trichloramine are formed. At pH values <5.5 monochloramine slowly converts to form dichloramine (Gray et al., 1979):



The relative proportions of monochloramine and dichloramine formed as a function of pH and temperature are listed in Table II-2.

Comparatively little is known about the physical properties of pure dichloramine because of its instability and difficulty of preparation. Its odor, volatility from aqueous solution, and relative solubility in various solvents are intermediate between those of monochloramine and trichloramine (NRC, 1980). Under equilibrium conditions at pH 4 it is the only product of the reaction of equimolar concentrations of chlorine and ammonia. Under normal conditions, however, dichloramine solutions are unstable (Corbett et al., 1953) and decompose by several mechanisms, not all of which have been elucidated (Chapin, 1931; Wei and Morris, 1974; Hand and Margerum, 1983).

Trichloramine (nitrogen trichloride) is formed in acid solutions where chlorine concentrations are much greater than those of ammonia. At these high chlorine concentrations and at pH values <3, trichloramine is the only chloramine present. Nitrogen

trichloride occurs in diminishing proportions at chlorine-to-ammonia mole ratios >2 and pH values of ≤ 7.5 . At pH >7.5 , no trichloramine is found, regardless of the ratio of chlorine to ammonia. Pure trichloramine is a bright yellow liquid that, because of its limited solubility, can be isolated from aqueous solution by solvent extraction (Dowell and Bray, 1917). Its chemical and physical properties are summarized in Table II-1. It can be explosive in concentrated solutions and is an effective chlorinating agent, particularly in nonaqueous media (Dowell and Bray, 1917; Jander, 1955; Kovacic et al., 1970). In aqueous solutions at neutral pH it decomposes slowly to ammonia and hypochlorous acid (Ryan et al., 1980) by an autocatalytic pathway (Hand and Margerum, 1983). Aqueous solutions of trichloramine are stabilized by small amounts of acid (Corbett et al., 1953).

When chlorine is added to waters containing ammonia, the breakpoint phenomenon becomes significant in the pH range of 6-9. The breakpoint is that dosage of chlorine that produces the first detectable amount of free chlorine residual. At chlorine-to-ammonia weight ratios of $<5:1$ ~pH 7, monochloramine is formed and the combined residual increases to a maximum. This is the case up to the hump in the curve as displayed in Figure II-1. At chlorine-to-ammonia weight ratios 5:1, dichloramine is formed. The residuals formed in this reaction occur between the top and the dip of the curve. With the addition of chlorine the previously formed dichloramine is oxidized to nitrous oxide (N_2O), nitrogen trichloride (NCl_3) and nitrogen (N_2). The formation of these nitrogen compounds oxidize chlorine which in turn results in a decrease of ammonia nitrogen. As the chlorine-to-ammonia nitrogen weight ratio reaches 10:1 at ~pH 7, the breakpoint

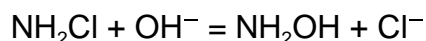
phenomenon occurs (NRC, 1980; White, 1972). At the breakpoint dosage, some resistant chloramines are present (primarily di- and trichloramine); however, they are not of any importance (NRC, 1980).

Chlorine that is added after the breakpoint exists as free chlorine [that is, elemental chlorine, hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-)] (Pressley et al., 1973; Wei and Morris, 1974). When natural waters and wastewater are chlorinated, there is a residual oxidant formed, which remains stable at the breakpoint and in the presence of hypochlorite beyond the breakpoint. This residual oxidant responds to conventional methods of analysis in the same way monochloramine does. It can be shown that some organic amino nitrogen compounds form very stable organic N-chloramines that, unlike inorganic chloramines, do not decompose in the presence of excess hypochlorite. This residual oxidant is, therefore, believed to be due to organic N-chloramines.

Monochloramine is less effective as a chlorinating agent than hypochlorous acid by a factor of $\sim 10^4$ (Morris, 1967). However, when chloramines (mostly monochloramine) were used to treat raw water, Stevens et al. (1978) determined that trihalomethane (THM) formation was minimized. Thus, during the chlorination of water, when the ammonia breakpoint is not achieved, THM production may be significantly reduced. Rickabaugh and Kinman (1978) determined that chloramination of Ohio River water with monochloramine at 10 mg/L, pH 7-9 and 25°C resulted in 90.7-99.9% less THM formation, as compared with THM production from chlorination with 10 mg/L chlorine as hypochlorous

acid or hypochlorite. Presumably many of the reaction products of water treated with free chlorine (Cl , OCl^- and HOCl) are produced by the reaction of combined chlorine residual (chlorinated waters that contain chloramines) with free chlorine. This is a result of the slow hydrolysis of chloramines to hypochlorous acid. The products should occur in low concentrations because of the low equilibrium concentration of the hypochlorous acid formed (Margerum et al., 1979).

Margerum et al. (1979) indicated that the formation of hydroxylamine (NH_2OH)

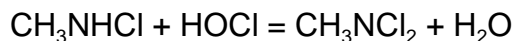


at pH 8 has a reaction half-time of 350 years. Therefore, it probably does not occur in water treatment.

When low concentrations (mg/L range) of monochloramine and phenol are mixed, chlorophenols appear after a reaction time of several days (Burttschell et al., 1959). This probably results from the hydrolysis of NH_2Cl and subsequent reaction of HOCl with phenols.

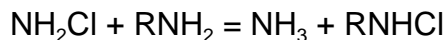
Organic amines and amino acids in natural waters also react rapidly with hypochlorite to form organic N-chloramines (Calvert, 1940; Wright, 1926, 1936; Taras, 1950; Crane et al., 1946; Ellis and Soper, 1954; Mauger and Soper, 1946; Sandford et al., 1971; Edmond

and Soper, 1949; Ingols et al., 1953; Wajon and Morris, 1980). Morris (1967) concluded that the reaction rates of free chlorine with amino nitrogen compounds increases with the basicity of the compound. As with ammonia, organic amines can also form dichloramines, but the reaction rates are considerably slower for the addition of the second chlorine atom than the addition of the first chlorine atom. Formation of N,N-dichloromethylamine from N-chloromethylamine occurs with a second order reaction rate constant at 25°C of $1.1 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ which is faster for organic than inorganic dichloramine (Morris, 1967):



Both inorganic chloramines and organic N-chloramines are formed when wastewater effluents are chlorinated. The relative amounts depend on the concentration ratios of ammonia to organic amino-N, the temperature, pH and the relative reaction rates (Isaac and Morris, 1980).

Organic N-chloramines can also form slowly by the reaction of inorganic chloramine with organic amines (Snyder and Margerum, 1982; Isaac and Morris, 1983, 1985):



The transfer of chlorine from monochloramine to organic amines has been shown to involve two mechanisms: hydrolysis of the monochloramine to ammonia and hypochlorous

acid and direct chlorine transfer from a protonated monochloramine NH_3Cl^+ to the organic amine (Snyder and Margerum, 1982; Isaac and Morris, 1983, 1985). Because the chlorine transfer reaction is slow, its significance may be limited to large water distribution systems using inorganic chloramine as the disinfectant where retention time in the system becomes considerable.

From a water treatment standpoint organic N-chloramines are undesirable, since they are not effective disinfectants (Feng, 1966; Marks and Styandskov, 1950; Wolfe et al., 1984; Wolfe and Olson, 1985).

Uses of Chloramines

The combining of ammonia with chlorine for the purpose of forming chloramines to treat drinking water has been called combined residual chlorination, chloramination or the chloramine process (NRC, 1979). This process has been employed to provide a more persistent disinfecting residual than free chlorine. It also generally reduces the unpleasant taste and odors resulting from the formation of chlorophenolic compounds (Symons et al., 1978).

Inorganic chloramines have been considered poorer disinfectants than hypochlorous acid, since nearly 25 times as much chloramine as free chlorine was required to obtain a 100% kill with equivalent contact times (Butterfield, 1948). Brodtmann and Russo (1979) refuted the idea that chloramine was a poor biocide for use in the treatment of drinking

water. They found that chloramine treatment of drinking water was effective in destroying ~60% of the total bacterial population remaining after clarification, with a contact time of <10 minutes. Furthermore, the chloramine treatment was effective in destroying ~88% of the remaining coliform bacteria before sand filtration. Thus, the authors concluded that chloramine properly applied at effective dosages (1.5-1.8 mg/L) produced 100% kills of pathogenic bacterial species and reduced the total population of bacteria to an acceptable range.

Analytical Methods

Methods deemed acceptable for the determination of chlorine residuals in natural and treated waters include the following: colorimetric methods, amperometric titration, stabilized neutral orthotolidine (SNORT) method, ferrous diethyl-p-phenylenediamine (DPD) method, and the leucocrystal violet (LCV) method.

The most common methods of analysis of monochloramine and most monochlorinated organic N-chloramines use the ability of these compounds to oxidize iodide to iodine followed by determination of the amount of iodine formed (APHA, 1980). The iodine formed can be titrated with a standardized solution of sodium thiosulfate and the endpoint detected visually with the aid of a starch solution. It can also be detected colorimetrically by addition of DPD (diethyl-p-phenylenediamine), which is converted to a red oxidized form. The intensity of the red color is measured with a spectrophotometer at 515 nm or with a filter photometer equipped with a filter having maximum transmission in the

wavelength range 490-530 nm. The oxidized DPD can also be titrated with standardized ferrous ammonium sulfate. This method is known as the FAS-DPD titrimetric method. Another method of measuring the iodine formed involves amperometric titration using a standardized solution of phenylarsine oxide. Leucocrystal violet is a colorless form of a dye that is converted by iodine to its colored form and measured with a spectrophotometer (592 nm), using a filter photometer or Nessler tubes.

Organic amines and albumenoid nitrogen compounds interfere with the analysis of monochloramine in chlorinated natural waters because they respond in a similar manner. In addition, as described below, the use of iodometric methods for analysis of chloramines has contributed a considerable amount of confusion to the meaning of the term "chloramines" (Johnson, 1978; Jolley and Carpenter, 1983; Wajon and Morris, 1980; Cooper et al., 1982). There is a need for new methods for distinguishing the various chemical compounds that respond to conventional analyses as "free residual chlorine" and "combined residual chlorine."

Most kinetic measurements of the formation, reactions and decomposition of inorganic mono-, di- and trichloramine have employed a direct spectrophotometric determination of their concentrations. Each has characteristic absorption spectra (Hand and Margerum, 1983). However, because of their low molar extinction coefficients the method is only good for measurements of solutions with concentrations $>10^{-4}$ M.

Evans (1982) reported a voltammetric method for analysis of inorganic chloramines in aqueous solution from pH 4-12. However, the method has approximately the same sensitivity as the spectrophotometric method.

Scully et al. (1984a) studied solutions of organic and inorganic N-chloramines in acid solution (pH 2) by cyclic voltammetry. Monochloramines can be distinguished from dichloramines and hypochlorous acid, but the method also lacks the sensitivity needed to measure concentrations $<10^{-4}$ M.

Scully et al. (1984b) developed a method for the analysis of organic and inorganic chloramines in dilute aqueous solution. The method involves derivatization of the chloramines with the sodium salt of 5-dimethylaminonaphthylene-1-sulfinic acid in bicarbonate buffer to form highly fluorescent sulfonamide derivatives. These derivatives can be separated by high pressure liquid chromatography so that organic chloramines can be measured in the presence of inorganic chloramine. The method has not yet been used successfully to identify organic N-chloramines in chlorinated natural waters. This will be necessary before the importance of organic N-chloramines in drinking water can be determined.

From a strictly chemical standpoint only ammonia and organic amines (R = alkyl or aryl) can form chloramines. Considerable confusion, however, has been introduced into the nomenclature of chloramines because of the methods used in the analysis of these

compounds in chlorinated natural waters and wastewaters (Johnson, 1978; Jolley and Carpenter, 1983; Wajon and Morris, 1980; Cooper et al., 1982). The term "combined residual chlorine" has been used to describe compounds in chlorinated waters that can be analyzed by amperometric and colorimetric methods only after addition of iodide, and the term "free residual chlorine" has been used to describe compounds that are generally analyzed by the same methods before the addition of iodide (APHA, 1980). Because solutions of organic and inorganic chloramines respond to these analyses as "combined residual chlorine" and because natural waters that contain high concentrations of ammonia form correspondingly high concentrations of combined residual chlorine, the terms combined residual chlorine and chloramines have become almost synonymous. Consequently, chlorinated waters that contain combined residual chlorine are said to contain chloramines. While the major fraction of combined residual chlorine is probably inorganic chloramines, other compounds including organic amines that are likely to contaminate natural waters and wastewaters react with chlorine to form compounds that respond to analyses as combined residual chlorine. For instance, proteinaceous or albumenoid nitrogen compounds contain amide linkages that react slowly with hypochlorite to form chloramides, $R(C=O)NCIR$, which respond to analyses as combined residual chlorine.

In addition, because solutions of hypochlorite are most commonly associated with free residual chlorine, hypochlorite and free residual chlorine also have become almost synonymous. Nevertheless, N-chlorosuccinimide, which is a chlorimide, and

trichloroisocyanuric acid respond at least partially to conventional analyses as free residual chlorine (Morris et al., 1980). The term free residual chlorine most accurately refers to elemental chlorine, hypochlorous acid (HOCl) and hypochlorite ion (OCl⁻). From a public health viewpoint these ambiguities can present serious problems; for instance, organic chloramines are poor disinfectants compared with inorganic chloramine (NH₂Cl) (Johnson, 1978). Jolley and Carpenter (1983) suggested the terms "combined oxidant" and "free oxidant" to avoid the ambiguities that have become associated with the residual chlorine term.

Further ambiguity exists in the term chloramine because it implies simply that a compound, organic or inorganic, contains both a chlorine atom and an amino nitrogen functional group. This would then include the highly carcinogenic nitrogen mustards that are not formed when water containing ammonia or organic amines is chlorinated. For the purposes of this document, only the toxicology and health effects data of organic and inorganic N-chlorinated amino nitrogen compounds will be reviewed.

Environmental Fate and Transport

The major source of chloramines in waters is the reaction of ammonia compounds with added chlorine. This occurs as a by-product of chlorination (i.e., in drinking water processing and sewage effluents) and from use of the chlorine-ammonia process (chloramination). An inventory of municipal water supplies undertaken in 1963 indicated that 308/11,590 surveyed used an ammonia-chlorine process (chloramination) (Moore and

Calabrese, 1980). For a discussion of rates of formation and breakdown of chloramines see the Physical and Chemical Properties Section and the Uses of Chloramines Section of this chapter. A 1984 survey of some U.S. utilities using chloramines (Trussell and Kreft, 1984) showed a possible distribution of chloramine residuals. A typical range of chloramine concentrations in drinking water supplies where it is used as a primary disinfectant or to provide a residual in the distribution system is 1.5-2.5 mg/L.

Summary

The alternate disinfectant inorganic chloramines are formed when water containing ammonia is chlorinated. The type and extent of each is dependent on pH, temperature and relative concentrations of ammonia and hypochlorite. Under the usual concentrations and conditions of water and wastewater treatment, monochloramine is the principal chloramine formed. Ammonia reacts with an excess of hypochlorous acid to form dichloramine or trichloramine. Dichloramine solutions, however, are unstable and readily decompose. When chlorine concentrations are much greater than ammonia and the solutions are acidic ($\text{pH} < 3$), trichloramine is formed. Monochloramine at standard temperature and pressure is a liquid, whereas trichloramine at standard temperature and pressure is a solid.

Organic amines or amino acids react rapidly with hypochlorite in natural waters to form organic N-chloramines. Organic N-chloramines are also formed by the slow reaction of

inorganic chloramines with organic amines. Information on organic chloramines and their reactions is very limited.

Chloramines are used primarily as disinfectants since they are a more persistent disinfecting residual than free chlorine. They also reduce the unpleasant taste and odors in drinking water resulting from chlorophenolic compound formation.

There are several acceptable methods for determining chlorine residuals in natural and treated waters. They are as follows: colorimetric methods, amperometric titration, stabilized neutral orthotolidine (SNORT) method, ferrous diethyl-p-phenylenediamine (DPD) method, and the leucocrystal violet (LCV) method. New methods with greater sensitivity and the ability to distinguish various chemical compounds are needed.

The reaction of ammonia compounds with added chlorine is the major source of chloramine release to the environment. This is due to processes and by-products of chlorination.

TABLE II-1		
Summary of Chemical and Physical Properties of Mono- and Trichloramines		
Properties	Monochloramine ^a	Trichloromine ^{b,c}
Chemical structure	NH ₂ Cl	NCI ₃
Molecular weight	51.48	120.38
Chemical Abstracts Registry Number	10599-90-3	10025-85-1
Registry of Toxic Effects of Chemical Substances (RTECS) Number	FN0275000	-
Synonyms	-	Nitrogen trichloride Nitrogen chloride Chlorine nitride Trichlorine nitride
Color	Yellow (liquid)	Yellow oil (liquid)
	Colorless crystals (solid)	Rhombic crystals (solid)
Physical state (25°C, 1 atm)	Liquid	Thick oil or rhombic crystals
Melting point, °C	-66°	<-40°
Boiling point, °C	-	<71° Explodes at 93°
Density	-	1.653
Solubility in water	Soluble	Insoluble in cold, decomposes in hot
Other solubilities	ETOH, ether, CCl ₄ , benzene	CS ₂ , PCl ₃ , benzene, CCl ₄ , CHCl ₃

^aRTECS, 1984

^bMerck Index, 1983

^cWeast, 1983

TABLE II-2

Proportions of Monochloramine (NH_2Cl) and Dichloramine (NHCl_2)
Formed in Water Chlorination with Equimolar Concentrations
of Ammonia and Chlorine^{a,b}

pH	Proportion (%) at 0°C		Proportion (%) at 10°C		Proportion (%) at 25°C	
	NH_2Cl	NHCl_2	NH_2Cl	NHCl_2	NH_2Cl	NHCl_2
4	0	100	0	100	0	100
5	34	66	20	80	13	87
6	77	23	67	33	57	43
7	94	6	81	9	88	12
8	99	1	98	2	97	3
9	100	0	100	0	100	0

^aSource: NRC, 1980

^bConsideration of kinetic effects leads to calculated values with lower proportions of NHCl_2

FIGURE II-1

Graphic Description of Breakdown Phenomenon